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Description

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Dye-Containing Pellets for Coloring Keratin Fibers

- 5 The present invention has for an object dye-containing pellets obtained by a special method of preparation, as well as the use of said pellets for coloring keratin fibers.

Direct dyes, nitro dyes and pigment dyes or oxidation dyes in the form of colorless developer/coupler precursors are the dyes usually employed for the coloring of keratin fibers.

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Dyes prepared according to the prior art are sold in conventional application forms. These application forms vary from liquid to creamy to waxy products. Aerosols, for example foam hair dyes, are also in use. According to the prior art, powdered dyes that must be mixed with an aqueous medium before use are also on the market.

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The aforesaid agents, however, are not satisfactory in every respect. For example, in the case of oil-treated, dust-free powders, the oils used have an adverse effect on product performance, whereas when reactive dyes and raw materials are used as well as in the case of powders and liquid systems, problems arise in terms of storage stability.

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Surprisingly, we were able, by means of a suitable method that is carried out with the aid of suitable carrier and encapsulation (coating) materials, to develop a dye-containing pellet for coloring keratin fibers which does not have the afore-described drawbacks and, in addition, provides better dosability and multicolor effects.

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Hence, the object of the present patent application is a dye-containing pellet which is obtained by (a) homogeneous mixing of a starting material containing at least one natural and/or synthetic dye with a suitable carrier material and then coating with a suitable encapsulation material or (b) coating a suitable carrier material with a mixture of at least one natural and/or synthetic dye and at least one suitable encapsulation material.

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The dye-containing pellets of the invention are prepared by the process based on extruder technology and schematically shown in Appendix 1 [pellets as under (a)] or by the top spray process [pellets as under (a) or (b)] schematically presented in Appendix 2.

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1. Preparation Based on Extruder Technology

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A base composition is prepared in a vertical granulator (rotor rotational speed = 50 to 200 rpm and preferably about 150 rpm; chopper rotational speed = 750 to 1250 rpm and preferably about 1000 rpm) at room temperature (15 to 35 °C) by dry mixing and then wet mixing the dye

composition with a carrier material and, optionally, antioxidants and other auxiliary agents. This base composition is then extruded from an extruder (rotational speed = 15 to 50 rpm and preferably about 25 to 30 rpm; screen mesh size = about 0.01 to 5 mm, preferably 0.1 to 3 mm and particularly 0.6 to 1 mm). The resulting granulate is rounded in a pelletizer (rotational speed = 400 to 800 rpm and preferably about 500 to 600 rpm). The granulate is then dried at a product temperature of 20 to 60 °C (preferably 30 to 55 °C) (incoming air temperature preferably about 70 to 80 °C) and then (optionally after previous warming to 40-50 °C) coated by the fluidized bed process (spraying rate preferably about 5 to 20 g/min; spraying air pressure preferably about 1.5 to 2.5 bar), the quantity of encapsulation material (based on the quantity of granulate to be coated) amounting to 0.5 to 50 weight percent, preferably 1 to 20 weight percent and particularly 2 to 15 weight percent. The product is finally dried (maximum product temperature about 51 °C).

2. Preparation by the Top Spray Process

(a) By this process, the dye composition is mixed with the carrier materials and optionally with antioxidants and other auxiliary agents in a fluidized bed granulator/coater (rotor rotational speed = 50 to 200 rpm and preferably about 150 rpm; chopper rotational speed = 750 to 1250 rpm and preferably about 1000 rpm) at room temperature (15 to 35 °C). The base composition thus obtained is then heated (maximum product temperature about 34 °C), then granulated and finally coated (spraying rate preferably about 6 to 20 g/min; spraying air pressure preferably about 0.25 to 0.75 bar), the quantity of encapsulation material used (based on the quantity of the granulate to be coated) amounting to 0.5 to 50 weight percent, preferably 1 to 20 weight percent and particularly 2 to 10 weight percent. If necessary, the product is then dried (maximum product temperature about 60 °C).

(b) The carrier materials and optionally the antioxidants and other auxiliary agents are mixed with one another in a fluidized bed granulator/coater (rotor rotational speed = 50 to 200 rpm and preferably about 150 rpm; chopper rotational speed = 750 to 1250 rpm and preferably about 1000 rpm) at room temperature (15 to 35 °C). The base composition thus obtained is then heated (maximum product temperature about 34 °C), then granulated and finally coated with a solution/dispersion of the dyes in a suitable encapsulation material (spraying rate preferably about 6 to 20 g/min; spraying air pressure preferably 0.25 to 0.75 bar), the quantity of encapsulation material used (based on the quantity of granulate to be coated) amounting to 0.5 to 50 weight percent, preferably 1 to 20 weight percent and particularly 2 to 10 weight percent. If necessary, the product is then dried (maximum product temperature about 57 °C).

Suitable carrier materials for the dye-containing pellets are powdered, microcrystalline substances which place the dye in a physical state that allows the process for the coating of the pellets with suitable encapsulation materials to be carried out. Suitable carrier materials are, in

particular, polyvinylpyrrolidone, dextrose, oligosaccharides, microcrystalline cellulose derivatives, for example hydroxypropylmethylcellulose, methylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, nonoxynol-hydroxyethylcellulose and cetylhydroxyethylcellulose, or physically or chemically modified starches or starch derivatives, for example starch esters (for example acetylated starches), starch ethers (for example hydroxalkylated starches), dialdehyde starches, dicarboxylstarches, distarch phosphates, hydroxyalkylstarch phosphates or hydroxyalkyl starches, wherein the alkyl groups preferably contain from 1 to 4 and more preferably 2 to 3 carbon atoms. Also suitable are crosslinked starch ethers, for example those bearing the INCI designations dimethylimidazolidone rice or corn starch, or hydrophobically modified starches (for example those bearing the INCI designation aluminum starch octenesuccinates). The starch can be modified thermally, hydrolytically or enzymatically, the starting starch possibly being obtained from known sources, for example corn, potatoes, sweet potatoes, peas, bananas, oats, wheat, barley, rice, sago, tapioca, taproot, amaranth, canna, sorghum etc. Particularly preferred starch derivatives are the nonionic starch derivatives, particularly the nonionic starch derivatives modified with an alkylene oxide such as ethylene oxide, propylene oxide or butylene oxide, or with acetic anhydride or butyl ketene dimer, and particularly with propylene oxide. Other suitable carrier materials are synthetic calcium silicate, diatomite, silicone dioxide or other free-flowing, non-caking powders.

Suitable encapsulation materials for the pellets of the invention are water-soluble or water-dispersible, film-forming substances which when spray-dried from solutions or dispersions are capable of depositing uniform films so that one can speak about encasing (coating). Suitable encapsulation materials are cellulose derivatives (for example methylcelluloses), polyethylene dispersions, polyacrylic acids, polyvinyl alcohols, polycarbonates, polyvinylpyrrolidone, polyesters and polyamides or natural film-formers, for example chitosan, shellac, oligosaccharides or Chinese balsam resin (colophony).

Suitable oxidation dye precursors are, for example, the following developers, couplers and self-coupling substances.

(i) *Developers:* 1,4-diaminobenzene (p-phenylenediamine), 1,4-diamino-2-methylbenzene (p-toluenediamine), 1,4-diamino-2,6-dimethylbenzene, 1,4-diamino-3,5-di-ethylbenzene, 1,4-diamino-2,5-dimethylbenzene, 1,4-diamino-2,3-dimethylbenzene, 2-chloro-1,4-diaminobenzene, 1,4-diamino-2-(thiophen-2-yl)benzene, 1,4-diamino-2-(thiophen-3-yl)benzene, 1,4-diamino-2-(pyridin-3-yl)benzene, 2,5-diaminobiphenyl, 1,4-diamino-2-methoxymethylbenzene, 1,4-diamino-2-aminomethylbenzene, 1,4-diamino-2-hydroxymethylbenzene, 1,4-diamino-2-(2-hydroxyethoxy)benzene, 2-[2-(acetylamino)ethoxy]-1,4-diaminobenzene, 4-phenylaminoaniline, 4-dimethylaminoaniline, 4-diethylaminoaniline, 4-dipropylaminoaniline, 4-[ethyl-(2-hydroxyethyl)amino]aniline, 4-[di(2-hydroxyethyl)amino]aniline, 4-[di(2-hydroxyethyl)amino]-2-methylaniline, 4-[(2-methoxyethyl)amino]aniline, 4-[(3-hydroxypropyl)amino]aniline, 4-[(2,3-dihydroxypropyl)amino]-

aniline, 1,4-diamino-2-(2-hydroxyethyl)benzene, 1,4-di-amino-2-(1-methylethyl)benzene, 1,3-bis[(4-aminophenyl)-(2-hydroxyethyl)amino]-2-propanol, 1,4-bis[(4-aminophenyl)amino]butane, 1,8-bis(2,5-di-aminophenoxy)-3,6-dioxaoctane, 4-aminophenol, 4-amino-3-methylphenol, 4-amino-3-(hydroxymethyl)phenol, 4-amino-3-fluorophenol, 4-methylaminophenol, 4-amino-2-(aminomethyl)phenol, 4-amino-2-(hydroxymethyl)phenol, 4-amino-2-fluorophenol, 4-amino-2-[(2-hydroxyethyl)amino]methylphenol, 4-amino-2-methylphenol, 4-amino-2-(methoxymethyl)phenol, 4-amino-2-(2-hydroxyethyl)phenol, 5-aminosalicylic acid, 2,5-diaminopyridine, 2,4,5,6-tetraaminopyrimidine, 2,5,6-triamino-4-(1H)-pyrimidone, 4,5-diamino-1-(2-hydroxyethyl)-1H-pyrazole, 4,5-diamino-1-(1-methylethyl)-1H-pyrazole, 4,5-diamino-1-[(4-methylphenyl)methyl]-1H-pyrazole, 1-[(4-chlorophenyl)methyl]-4,5-diamino-1H-pyrazole, 4,5-diamino-1-methyl-1H-pyrazole, 2-aminophenol, 2-amino-6-methyl-phenol and 2-amino-5-methylphenol, alone or in admixture with one another.

(ii) *Couplers:* N-(3-dimethylaminophenyl)urea, 2,6-diaminopyridine, 2-amino-4-[(2-hydroxyethyl)amino]anisole, 2,4-diamino-1-fluoro-5-methylbenzene, 2,4-diamino-1-methoxy-5-methylbenzene, 2,4-diamino-1-ethoxy-5-methylbenzene, 2,4-diamino-1-(2-hydroxyethoxy)-5-methylbenzene, 2,4-di[(2-hydroxyethyl)amino]-1,5-dimethoxybenzene, 2,3-diamino-6-methoxypyridine, 3-amino-6-methoxy-2-(methylamino)pyridine, 2,6-diamino-3,5-dimethoxypyridine, 3,5-diamino-2,6-dimethoxypyridine, 1,3-diaminobenzene, 2,4-diamino-1-(2-hydroxyethoxy)benzene, 1,3-diamino-4-(2,3-dihydroxypropoxy)benzene, 2,4-diamino-1,5-di(2-hydroxyethoxy)benzene, 1-(2-aminoethoxy)-2,4-diaminobenzene, 2-amino-1-(2-hydroxyethoxy)-4-methylaminobenzene, 2,4-diaminophenoxyacetic acid, 3-[di(2-hydroxyethyl)amino]aniline, 4-amino-2-di[(2-hydroxyethyl)amino]-1-ethoxybenzene, 5-methyl-2-(1-methylethyl)phenol, 3-[(2-hydroxyethyl)amino]aniline, 3-[(2-aminoethyl)amino]aniline, 1,3-di(2,4-diaminophenoxy)propane, di(2,4-diaminophenoxy)methane, 1,3-diamino-2,4-dimethoxybenzene, 2,6-bis(2-hydroxyethyl)aminotoluene, 4-hydroxyindole, 3-dimethylaminophenol, 3-diethylaminophenol, 5-amino-2-methylphenol, 5-amino-4-fluoro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-ethoxy-2-methylphenol, 3-amino-2,4-dichlorophenol, 5-amino-2,4-dichlorophenol, 3-amino-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-aminophenol, 2-[(3-hydroxyphenyl)amino]acetamide, 5-[(2-hydroxyethyl)amino]-4-methoxy-2-methylphenol, 5-[(2-hydroxyethyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-phenol, 3-[(2-methoxyethyl)amino]phenol, 5-amino-2-ethylphenol, 5-amino-2-methoxyphenol, 2-(4-amino-2-hydroxyphenoxy)ethanol, 5-[(3-hydroxypropyl)amino]-2-methylphenol, 3-[(2,3-dihydroxypropyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-2-methylphenol, 2-amino-3-hydroxypyridine, 5-amino-4-chloro-2-methylphenol, 1-naphthol, 2-methyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2-methyl-1-naphthol acetate, 1,3-dihydroxybenzene, 1-chloro-2,4-dihydroxybenzene, 2-chloro-1,3-dihydroxybenzene, 1,2-dichloro-3,5-dihydroxy-4-methylbenzene, 1,5-dichloro-2,4-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 3,4-methylenedioxyphephenol, 3,4-methylenedioxyaniline, 5-[(2-hydroxyethyl)amino]-1,3-benzodioxole, 6-bromo-1-hydroxy-3,4-methylenedioxobenzene, 3,4-diaminobenzoic acid, 3,4-dihydro-6-hydroxy-1,4(2H)-benzoxazine, 6-amino-3,4-dihydro-1,4(2H)-

benzoxazine, 3-methyl-1-phenyl-5-pyrazolone, 5,6-dihydroxyindole, 5,6-dihydroxyindoline, 5-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole and 2,3-indolinedione, alone or in admixture with one another.

- 5 (iii) *Self-coupling compounds*: 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-ethoxyphenol or 2-propylamino-5-aminopyridine.

Among the aforesaid oxidation dyes [sic], the following compounds, alone or in combination with one another, are particularly preferred: 2,5-diaminotoluene, 2,4-diaminophenoxyethanol, resorcinol, 2-methylresorcinol, m-aminophenol, 4-amino-m-cresol, 4-amino-2-hydroxytoluene, 6-amino-m-cresol, 2-amino-4-hydroxyethylaminoanisol, 1-naphthol, hydroxyethyl-3,4-methylene-dioxyaniline, 2,5-diaminophenylethanol, N,N-bis(2-hydroxyethyl)-p-phenylenediamine, phenylmethylpyrazolone, 1-hydroxyethyl-4,5-diaminopyrazole and 2-amino-6-chloro-4-nitrophenol or the salts thereof.

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The total quantity of oxidation precursors present in the pellets of the invention amounts to about 0.1 to 70 weight percent and particularly about 0.5 to 50 weight percent.

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To achieve certain color shades, it is also possible to use common natural and/or synthetic direct dyes, for example vegetable dyes such as henna or indigo, triphenylmethane dyes, aromatic nitro dyes, azo dyes, quinone dyes, cationic dyes or anionic dyes.

It is also possible for the pellets of the invention to contain exclusively direct dyes, namely without added oxidation precursors.

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Suitable synthetic dyes are, for example: hydroxyethyl-2-nitro-p-toluidine, 2-hydroxyethylpicramic acid, 4-nitrophenylaminourea, tri(4-amino-3-methylphenyl)carbenium chloride (Basic Violet 2), 1,4-diamino-9,10-anthracenedione (Disperse Violet 1), 1,4-bis[(2-hydroxyethyl)amino]-2-nitrobenzene, 1-(2-hydroxyethyl)amino-2-nitro-4-[di(2-hydroxyethyl)amino]benzene (HC Blue No. 2), 1-amino-3-methyl-4-[(2-hydroxyethyl)amino]-6-nitrobenzene (HC Violet No. 1), 4-[ethyl-(2-hydroxyethyl)amino]-1-[(2-hydroxyethyl)amino]-2-nitrobenzene hydrochloride (HC Blue No. 12), 4-[di(2-hydroxyethyl)amino]-1-[(2-methoxyethyl)amino]-2-nitrobenzene (HC Blue No. 11), 1-[(2,3-dihydroxypropyl)amino]-4-[methyl-(2-hydroxyethyl)amino]-2-nitrobenzene (HC Blue No. 10), 1-[(2,3-dihydroxypropyl)amino]-4-[ethyl-(2-hydroxyethyl)amino]-2-nitrobenzene hydrochloride (HC Blue No. 9), 1-(3-hydroxypropylamino)-4-[di(2-hydroxyethyl)amino]-2-nitrobenzene (HC Violet No. 2), 1-methylamino-4-[methyl-(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Blue No. 6), 2-[(4-amino-2-nitrophenyl)amino]-5-dimethylaminobenzoic acid (HC Blue No. 13), 1-amino-4-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Red No. 7), 2-amino-4,6-dinitrophenol, 4-amino-2-nitrodiphenylamine (HC Red No. 1), 1-amino-4-[di(2-hydroxyethyl)amino]-2-nitrobenzene hydrochloride (HC Red No. 13), 1-amino-5-chloro-4-[(2-hydroxyethyl)amino]-2-nitrobenzene, 4-amino-

1-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Red. No. 3), 4-amino-3-nitrophenol, 4-[(2-hydroxyethyl)amino]-3-nitrophenol, 1-[(2-aminoethyl)amino]-4-(2-hydroxyethoxy)-2-nitrobenzene (HC Orange No. 2), 4-(2,3-dihydroxypropoxy)-1-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Orange No. 3), 1-amino-5-chloro-4-[(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Red No. 10), 5-chloro-1,4-[di-(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Red No. 11), 2-[(2-hydroxyethyl)amino]-4,6-dinitrophenol, 4-ethylamino-3-nitrobenzoic acid, 2-[(4-amino-2-nitrophenyl)amino]benzoic acid, 2-chloro-6-ethylamino-4-nitrophenol, 2-amino-6-chloro-4-nitrophenol, 4-[(3-hydroxypropyl)amino]-3-nitrophenol, 2,5-diamino-6-nitropyridine, 1,2,3,4-tetrahydro-6-nitroquinoxaline, 7-amino-3,4-dihydro-6-nitro-2H-1,4-benzoxazine (HC Red No. 14), 1-amino-2-[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 5), 1-(2-hydroxyethoxy)-2-[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 4), 1-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Yellow No. 2), 2-[(2-hydroxyethyl)amino]-1-methoxy-5-nitrobenzene, 2-amino-3-nitrophenol, 1-(2-hydroxyethoxy)-3-methylamino-4-nitrobenzene, 2,3-(dihydroxypropoxy)-3-methylamino-4-nitrobenzene, 2-[(2-hydroxyethyl)amino]-5-nitrophenol (HC Yellow No. 11), 3-[(2-aminoethyl)amino]-1-methoxy-4-nitrobenzene hydrochloride (HC Yellow No. 9), 1-[(2-ureidoethyl)amino]-4-nitrobenzene, 4-[(2,3-dihydroxypropyl)amino]-3-nitro-1-trifluoromethylbenzene (HC Yellow No. 6), 1-chloro-2,4-bis[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 10), 4-[(2-hydroxyethyl)amino]-3-nitro-1-methylbenzene, 1-chloro-4-[(2-hydroxyethyl)amino]-3-nitrobenzene (HC Yellow No. 12), 4-[(2-hydroxyethyl)amino]-3-nitro-1-trifluoromethylbenzene (HC Yellow No. 13), 4-[(2-hydroxyethyl)amino]-3-nitrobenzonitrile (HC Yellow No. 14), 4-[(2-hydroxyethyl)amino]-3-nitrobenzamide (HC Yellow No. 15), 1,4-di[(2,3-dihydroxypropyl)amino]-9,10-anthraquinone, 1-[(2-hydroxyethyl)amino]-4-methylamino-9,10-anthraquinone (C.I. 61505, Disperse Blue No. 3), 2-[(2-aminoethyl)amino]-9,10-anthraquinone (HC Orange No. 5), 1-hydroxy-4-[(4-methyl-2-sulfophenyl)amino]-9,10-anthraquinone, 1-[(3-aminopropyl)amino]-4-methylamino-9,10-anthraquinone (HC Blue No. 8), 1-[(3-aminopropyl)amino]-9,10-anthraquinone (HC Red No. 8), 1,4-diamino-2-methoxy-9,10-anthraquinone (C.I. 62015, Disperse Red No. 11, Solvent Violet No. 26), 1,4-dihydroxy-5,8-bis[(2-hydroxyethyl)amino]-9,10-anthraquinone (C.I. 62500, Disperse Blue No. 7, Solvent Blue No. 69), 9-(dimethylamino)benzo[a]-phenoxyazin-7-i um chloride (C.I. 51175; Basic Blue No. 6), di[4-(diethylamino)phenyl][4-(ethylamino)naphthyl]carbenium chloride (C.I. 42595; Basic Blue No. 7), 3,7-di(dimethylamino)phenoxyazin-5-i um chloride (C.I. 52015; Basic Blue No. 9), di[4-(dimethylamino)phenyl][4-(phenylamino)naphthyl]carbenium chloride (C.I. 44045; Basic Blue No. 26), 2-[(4-(ethyl-(2-hydroxyethyl)amino)phenyl)azo]-6-methoxy-3-methylbenzothiazolium methylsulfate (C.I. 11154; Basic Blue No. 41), 8-amino-2-bromo-5-hydroxy-4-imino-6-[(3-trimethylammonio)phenyl]amino]-1(4H)-naphthalenone chloride (C.I. 56059; Basic Blue No. 99), bis[4-(dimethylamino)phenyl][4-(methylamino)phenyl]carbenium chloride (C.I. 42535; Basic Violet No. 1), tris[4-(dimethylamino)phenyl]carbenium chloride (C.I. 42555; Basic Violet No. 3), 2-[3,6-(diethylamino)dibenzopyranium-9-yl]benzoyl chloride (C.I. 45170; Basic Violet No. 10), di(4-aminophenyl)-(4-amino-3-methylphenyl)carbenium chloride (C.I. 42510; Basic Violet No. 14), 1,3-bis[(2,4-diamino-5-methylphenyl)azo]-3-methylbenzene (C.I. 21010; Basic Brown No. 4), 1-[(4-aminophenyl)azo]-7-(trimethylammonio)-2-naphthol chloride (C.I. 12250; Basic Brown No. 16),

1-[(4-amino-2-nitro-phenyl)azo]-7-(trimethylammonio)-2-naphthol chloride (Basic Brown No. 17),
1-[(4-amino-3-nitrophenyl)azo]-7-(trimethylammonio)-2-naphthol chloride (C.I. 12251; Basic
Brown No. 17), [sic], 3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride (C.I. 50240; Basic
Red. No. 2), 1,4-dimethyl-5-{{[4-(dimethylamino)phenyl]azo}-1,2,4-triazolium chloride (C.I. 11055;
5 Basic Red No. 22), 2-hydroxy-1-[(2-methoxyphenyl)azo]-7-(trimethylammonio)-naphthalene chlo-
ride (C.I. 12245; Basic Red No. 76), 2-{2-[(2,4-dimethoxyphenyl)amino]ethenyl}-1,3,3-trimethyl-
3H-indol-1-i um chloride (C.I. 48055; Basic Yellow No. 11), 3-methyl-1-phenyl-4-{{[3-(trimethyl-
10 ammonio)phenyl]azo}pyrazol-5-one chloride (C.I. 12719; Basic Yellow No. 57), bis[4-(diethyl-
amino)phenyl]phenylcarbenium hydrogen sulfate (1:1) (C.I. 42040; Basic Green No. 1), 1-[di-(2-
hydroxyethyl)amino]-3-methyl-4-[(4-nitrophenyl)azo]benzene (C.I. 11210, Disperse Red No. 17),
4-[(4-aminophenyl)azo]-1-[di-(2-hydroxyethyl)amino]-3-methylbenzene (HC Yellow No. 7), 2,6-di-
15 amino-3-[(pyridin-3-yl)-azo]pyridine, disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalene-
sulfonate (C.I. 15985; Food Yellow No. 3; FD&C Yellow No. 6), disodium 2,4-dinitro-1-naphthol-7-
sulfonate (C.I. 10316; Acid Yellow No. 1; Food Yellow No. 1), 2-(indan-1,3-dion-2-yl)-quinolin-x,x-
sulfonic acid (mixture of mono- and disulfonic acid) (C.I. 47005; D&C Yellow No. 10; Food Yellow
No. 13; Acid Yellow No. 3), trisodium 5-hydroxy-1-(4-sulfophenyl)-4-[(4-sulfophenyl)azo]pyrazole-
20 3-carboxylate (C.I. 19140; Food Yellow No. 4; Acid Yellow No. 23), 9-(2-carboxyphenyl)-6-hy-
droxy-3H-xanthen-3-one (C.I. 45350; Acid Yellow No. 73; D&C Yellow No. 8), sodium 5-[(2,4-di-
nitrophenyl)amino]-2-phenylaminobenzene-sulfonate (C.I. 10385; Acid Orange No. 3), mono-
25 sodium 4-[(2,4-dihydroxyphenyl)-azo]benzenesulfonate (C.I. 14270; Acid Orange No. 6), sodium
4[(2-hydroxynaphth-1-yl)azo]benzenesulfonate (C.I. 15510; Acid Orange No. 7), sodium 4-[(2,4-
dihydroxy-3-[(2,4-dimethylphenyl)azo]phenyl)azo]benzenesulfonate (C.I. 20170; Acid Orange No.
24), disodium 4-hydroxy-3-[(4-sulfonaphth-1-yl)azo]-1-naphthalenesulfonate (C.I. 14720; Acid
Red No. 14), trisodium 6-hydroxy-5-[(4-sulfonaphth-1-yl)azo]-2,4-naphthalenedisulfonate (C.I.
30 16255; Ponceau 4R; Acid Red No. 18), trisodium 3-hydroxy-4-[(4-sulfonaphth-1-yl)azo]-2,7-
naphthalenedisulfonate (C.I. 16185; Acid Red No. 27), disodium 8-amino-1-hydroxy-2-
(phenylazo)-3,6-naphthalenedisulfonate (C.I. 17200; Acid Red No. 33), disodium 5-(acetylamino)-
4-hydroxy-3-[(2-methylphenyl)azo]-2,7-naphthalenedisulfonate (C.I. 18065; Acid Red No. 35),
disodium 2-(3-hydroxy-2,4,5,7-tetraiododibenzopyran-6-on-9-yl)benzoate (C.I. 45430; Acid Red
35 No. 51), N-[6-(diethylamino)-9-(2,4-disulfophenyl)-3H-xanthen-3-ylidene]-N-ethylethaneammo-
ni um hydroxide inner salt, sodium salt (C.I. 45100; Acid Red No. 52), disodium 8-{{[4-
(phenylazo)phenyl]azo}-7-naphthol-1,3-disulfonate (C.I. 27290; Acid Red No. 73); 2',4',5',7'-
40 tetrabromo-3',6'-dihydroxyspiro{isobenzofuran-1(3H),9-[9H]xanthen}-3-one disodium salt (C.I.
45380; Acid Red No. 87), 2',4',5',7'-tetrabromo-4,5,6,7-tetrachloro-3',6'-dihydroxyspiro-
{isobenzofuran-1-3H),9'[9H]-xanthen}-3-one disodium salt (C.I. 45410; Acid Red No. 92), 3',6'-
dihydroxy-4',5'-diiodo-spiro{isobenzofuran-1(3H),9(9H)-xanthen}-3-one disodium salt (C.I. 45425;
Acid Red No. 95), (2-sulfophenyl)di[4-(ethyl((4-sulfophenyl)methyl)amino)phenyl]carbenium
disodium salt, betaine (C.I. 42090; Acid Blue No. 9; FD&C Blue No. 1), 1,4-bis[(2-sulfo-4-meth-
ylphenyl)amino]-9,10-anthraquinone disodium salt (C.I. 61 570; Acid Green No. 25), bis[4-
(dimethylamino)phenyl]-(3,7-disulfo-2-hydroxynaphth-1-yl)carbenium inner salt, monosodium salt

(C.I. 44090; Food Green No. 4; Acid Green No. 50), bis[4-(diethyl-amino)phenyl](2,4-di-sulfophenyl)carbenium inner salt, sodium salt (2:1) (C.I. 42045; Food Blue No. 3; Acid Blue No. 1), bis[4-[diethylamino]phenyl](5-hydroxy-2,4-disulfophenyl)carbenium inner salt, calcium salt (2:1) (C.I. 42051; Acid Blue No. 3), sodium 1-amino-4-(cyclohexylamino)-9,10-anthraquinone-2-sulfonate (C.I. 62045; Acid Blue No. 62), disodium 2-(1,3-dihydro-3-keto-5-sulfo-2H-indol-2-ylidene)-2,3-dihydro-3-keto-1H-indol-5-sulfonate (C.I. 73015; Acid Blue No. 74), 9-(2-carboxy-phenyl)-3-[(2-methylphenyl)amino]-6-[(2-methyl-4-sulfophenyl)amino]xanthylium inner salt, mono-sodium salt (C.I. 45190; Acid Violet No. 9), 1-hydroxy-4-[(4-methyl-2-sulfophenyl)amino]-9,10-anthraquinone sodium salt (C.I. 60730; D&C Violet No. 2; Acid Violet No. 43), bis{3-nitro-4-[(4-phenylamino)-3-sulfophenylamino]phenyl} sulfone (C.I. 10410; Acid Brown No. 13), disodium 5-amino-4-hydroxy-6-[(4-nitrophenyl)azo]-3-(phenylazo)-2,7-naphthalenedisulfonate (C.I. 20470; Acid Black No. 1), 3-hydroxy-4-[(2-hydroxynaphth-1-yl)azo]-7-nitro-1-naphthalenesulfonic acid chromium complex (3:2) (C.I. 15711); Acid Black No. 52), disodium 3-[(2,4-dimethyl-5-sulfophenyl)azo]-4-hydroxy-1-naphthalenesulfonate (C.I. 14700; Food Red No. 1; FD&C Red No. 4), tetrasodium 4-(acetylamino)-5-hydroxy-6-[(7-sulfo-4-[(4-sulfophenyl)azo]naphth-1-yl)azo]-1,7-naphthalenedisulfonate (C.I. 28440; Food Black No. 1) and sodium 3-hydroxy-4-(3-methyl-5-keto-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl-azo)naphthalene-1-sulfonate, chromium complex (Acid Red No. 195), 3',3",4,5,5',5",6,7-octabromophenolsulfonphthalein (Tetrabromophenol Blue), 1-((4-amino-3,5-dimethylphenyl)-(2,6-dichlorophenyl)methylene)-3,5-dimethyl-4-imino-2,5-cyclohexadiene combined with phosphoric acid (1:1) (Basic Blue 77), 2',4',5',7'-tetrabromo-4,5,6,7-tetrachloro-3',6'-dihydroxyspiro{isobenzofuran-1-(3H),9'[9H]xanthen}-3-one disodium salt (Acid Red No. 92), N,N-di(2-hydroxyethyl)-3-methyl-4-[(4-nitrophenyl)azo]aniline (Disperse Red 17), disodium 2,4-dinitro-1-naphthol-7-sulfonate (Acid Yellow 1), sodium 4-[(2-hydroxynaphthalen-1-yl)azo]-benzenesulfonate (Acid Orange 7), 2-((4-(ethyl-(2-hydroxyethyl)amino)-2-methylphenyl)azo)-5-nitro-1,3-thiazole (Disperse Blue 106), 2,4-dinitro-1-naphthol, 2-[(4-aminophenyl)azo]-1,3-dimethyl-1H-imidazol-3-i um chloride, 1-methyl-4-[(methylphenylhydrazone)methyl]pyridinium methosulfate, 2-[(4-(dimethylamino)phenyl)azo]-1,3-dimethylimidazolium chloride, 2-((4-((4-methoxy-phenyl)amino)phenyl)azo)-1,3-dimethyl-1H-imidazol-3-i um chloride and 1,3-dimethyl-2-((4-((phenylmethyl)amino)phenyl)azo)-1H-imidazol-3-i um chloride, alone or in combination with one another.

Particularly preferred among the aforesaid direct dyes are the following compounds, alone or in combination with one another: hydroxyethyl-2-nitro-p-toluidine, 2-hydroxyethylpicramic acid, 4-nitrophenylaminourea, tri(4-amino-3-methylphenyl)carbenium chloride (Basic Violet 2), 1,4-di-amino-9,10-anthracenedione (Disperse Violet 1), 1-(2-hydroxy-ethyl)amino-2-nitro-4-[di(2-hydroxyethyl)amino]benzene (HC Blue No. 2), 4-[ethyl-(2-hydroxyethyl)amino]-1-[(2-hydroxyethyl)amino]-2-nitrobenzene hydrochloride (HC Blue No. 12), 1-amino-4-[di(2-hydroxyethyl)amino]-2-nitrobenzene hydrochloride (HC Red No. 13), 4-amino-1-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Red No. 3), 4-amino-3-nitrophenol, 4-[(2-hydroxyethyl)amino]-3-nitrophenol,

1-amino-5-chloro-4-[(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Red No. 10), 5-chloro-1,4-[di(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Red No. 11), 2-chloro-6-ethylamino-4-nitrophenol, 2-amino-6-chloro-4-nitrophenol, 4-[(2-hydroxyethyl)amino]-3-nitro-1-trifluoromethylbenzene (HC Yellow No. 13), 8-amino-2-bromo-5-hydroxy-4-imino-6-[(3-(trimethylammonio)phenyl]amino}-1(4H)-naphthalenone chloride (C.I. 56059; Basic Blue No. 99), 1-[(4-amino-phenyl)azo]-7-(trimethylammonio)-2-naphthol chloride (C.I. 12250; Basic Brown No. 16), 1-[(4-amino-2-nitrophenyl)azo]-7-(trimethylammonio)-2-naphthol chloride (Basic Brown No. 17), 2-hydroxy-1-[(2-methoxyphenyl)azo]-7-(trimethylammonio)naphthalene chloride (C.I. 12245; Basic Red No. 76), 3-methyl-1-phenyl-4-[(3-(trimethylammonio)phenyl]azo]pyrazol-5-one chloride (C.I. 12719; Basic Yellow No. 57) and 2,6-diamino-3-[(pyridin-3-yl)azo]pyridine as well as the salts thereof.

The total quantity of direct dyes in the pellets of the invention amounts to about 0.1 to 90 weight percent and preferably 1 to 70 weight percent.

Other known and common dyes used in hair colorants are described in, among other publications, E. Sagarin "Cosmetics, Science and Technology", Interscience Publishers Inc., New York (1957), pages 503 ff, in H. Janistyn, "Handbuch der Kosmetika und Riechstoffe" [Manual of Cosmetics and Fragrances], vol. 3 (1973), pages 388 ff, and in K. Schrader "Grundlagen und Rezepturen der Kosmetika" [Fundamentals and Formulations of Cosmetics], 2nd edition (1989), pages 782-815, the disclosures of which are hereby included by reference.

The dye-containing pellets of the invention have many advantages. They are absolutely dust-free, but do not have the drawbacks presented by the common dust-free, oil-treated powders and, in particular, do not exert an adverse effect on product performance. Depending on the kind and layer thickness of the selected coating material, the release of the dyes is possible at any desired point in time (delayed release). Also possible is the use of reactive dyes together with reactive raw materials (for example oxidants such as the persulfates and hydrogen peroxide salts or hydrogen peroxide addition products) as well as a clearly improved storage stability compared to powders and aqueous/alcoholic systems. Of particular interest is the possibility of uncomplicated achievement of multicolor effects through the kind and layer thickness of the selected coating material, whereas according to the current state of the art such multicolor effects can be attained only by extremely time-consuming and complicated techniques, for example by sheet or strand techniques. In addition, the pellets of the invention have clearly better dosability than do prior-art colorants (powders, aqueous/alcoholic systems).

Other objects of the present invention therefore are the use of the aforesaid pellets for producing colorants for keratin fibers and an agent for coloring keratin fibers, for example hair and particularly human hair, which is prepared by mixing the aforesaid pellets with an aqueous or aqueous-alcoholic preparation.

The aqueous or aqueous-alcoholic preparation used can be either water or a mixture of water and a C₁-C₆ alcohol (for example, ethanol or isopropanol) or a common hydrogen peroxide solution or hydrogen peroxide emulsion or else a common hair cleaning agent, hair conditioner or hair-firming agent.

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The composition of such preparations is known and can be found in pertinent text books on cosmetics, for example in Karlheinz Schrader "Grundlagen und Rezepturen der Kosmetika" [Fundamentals and Formulations of Cosmetics], 2nd edition (1989) which is hereby included by reference.

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For example, the colorant of the invention can contain antioxidants, for example ascorbic acid, thioglycolic acid or sodium sulfite, as well as complexing agents for heavy metals, for example an ethylenediaminetetraacetate or nitriloacetic acid, in an amount of up to about 0.5 weight percent.

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Perfume oils can be contained in the dye carrier composition of the invention in an amount of up to about 1 weight percent. Moreover, the afore-described hair colorant can optionally contain other auxiliary agents and additives commonly used in such colorants, for example thickeners, for example homopolymers of acrylic acid, vegetable gums, algal polysaccharides, amphiphilic associative thickeners; furthermore preservatives; complexing agents; wetting agents or emulsifiers from the classes of anionic, cationic, amphoteric or nonionic surface-active substances; alkalinizing agents (for example ammonium salts, or amino acids such as glycine and alanine) furthermore hair-care agents, such as cationic polymers or resins, lanolin derivatives, cholesterol, vitamins, pantothenic acid and betaine. The said constituents are employed in amounts normally used for such purposes, for example the wetting agents and emulsifiers at a concentration from 0.1 to 30 weight percent and the hair-care agents at a concentration from 0.1 to 5.0 weight percent.

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The colorants containing oxidation dye precursors are used in combination with one or more known chemical oxidants, for example hydrogen peroxide or a salt or adduct thereof, as well as persulfates such as sodium persulfate, potassium persulfate or ammonium persulfate, or they are activated by air oxidation (optionally in the presence of appropriate enzymes or catalysts). If simultaneous brightening and coloring of the fibers is desired, it is also possible to use colorants based on direct dyes - provided said dyes are sufficiently oxidation-resistant - in combination with one or more known oxidants, for example hydrogen peroxide or a salt or adduct thereof as well as persulfates such as sodium persulfate, potassium persulfate or ammonium persulfate.

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To attain simultaneous brightening of the fibers, the dye-containing pellets of the invention can also contain an ammonium carbonate, for example ammonium hydrogen carbonate, or an amino acid or a salt thereof, for example sodium glycinate.

The following examples will explain the subject matter of the invention in greater detail without limiting its scope to these examples.

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E x a m p l e s

Example 1: Preparation of Dye Pellets by the Top Spray Method

In a Glatt fluidized bed granulator and coater, the following mixture A was heated to a product temperature of 34 °C with air at an incoming air temperature of 90 °C and an air flow rate of 18
10 m³/h.

Mixture A

15	381.2 g	of 4-(2-hydroxyethylamino)-3-nitrophenol
	101.0 g	of 2-[(2-hydroxyethyl)amino]-4,6-dinitrophenol
	100.0 g	of corn starch

A 20 % aqueous polyvinylpyrrolidone solution ("spraying solution") was then sprayed onto this
20 mixture at an initial spraying rate of 8 g/min and at a spraying air pressure of 0.5 bar. In the course of the granulation process, the spraying rate was increased to 12 g/min and the incoming air temperature was increased to 100 °C, while the air flow rate was raised to a maximum of 30 m³/h. The product temperature was kept at about 30-31 °C throughout the entire procedure.
25 After 310 g had been sprayed on, the pellets were dried at a maximum product temperature of 57 °C and then cooled to about 30 °C and screened.

Example 2: Preparation of Dye Pellets by Extruder Technology

Mixture A

30	1896 g	of 4-(2-hydroxyethylamino)-3-nitrophenol
	504 g	of 2-[(2-hydroxyethyl)amino]-4,6-dinitrophenol
	800 g	of microcrystalline cellulose
35	800 g	of corn starch

Mixture A was mixed in a vertical granulator (rotor rotational speed = about 150 rpm; chopper rotational speed = about 1000 rpm) for 1 minute and then, by means of a dual nozzle and with continuing mixing, sprayed with 2091 g of a 6 % aqueous hydroxypropylmethylcellulose solution.
40 The composition thus obtained was extruded from a BR 200-type extruder (rotational speed = 27

rpm; screen mesh diameter: 1.0 mm) at a product temperature of about 30 °C. The material thus obtained was then rounded in a P 50-type pelletizer for 1 minute at 550 rpm and then dried in a Glatt vertical granulator at an incoming air temperature of 70 °C, an air flow rate of about 60-90 m³/h and a maximum product temperature of 51 °C.

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In a Glatt fluidized bed granulator and coater, 1500 g of the dried dye pellets was heated at an incoming air temperature of about 50 °C and an air flow rate of 75 m³/h to a product temperature of 39-40 °C. The pellets were then sprayed with a 10 % aqueous solution of hydroxypropylmethylcellulose at a spraying rate of 5 g/min and a spraying air pressure of 2.5 bar. In the course of the procedure, the spraying rate was increased to 8.5 g/min. After 2215 g of the spraying solution had been applied, corresponding to an addition of 14% of solids, the material was again dried at a maximum product temperature of 51 °C (incoming air temperature = about 70 °C), and then cooled to about 27 °C and screened.

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15 (Alternatively the drying and coating or the granulation, drying and coating can be carried out in the same processing step).

Example 3: *Preparation of Dye Pellets by Extruder Technology;
Gold Color Shade*

Mixture A

2400 g	of 2-amino-6-chloro-4-nitrophenol
800 g	of microcrystalline cellulose
800 g	of corn starch

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Mixture A was pelletized as in Example 2, but by using a 5.6% aqueous hydroxypropylmethylcellulose solution as the coating agent.

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Example 4: *Preparation of Dye Pellets by Extruder Technology;
Red/Mahogany Color Shade*

Mixture A

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1896 g	of 3-nitro-p-hydroxyethylaminophenol
504 g	of 2-hydroxyethylpicramic acid
800 g	of microcrystalline cellulose
800 g	of potato starch

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The preparation was carried out as described in Example 2, but by using a 6.25% aqueous hydroxymethylcellulose solution as the coating agent.

5 **Example 5:** *Preparation of Dye Pellets by Extruder Technology*

Mixture A

10	1411 g	of 2,5-diaminotoluene sulfate
	636 g	of 4-amino-2-hydroxytoluene
	353 g	of 2-amino-4-(β-hydroxyethylamino)anisole sulfate
	794 g	of ascorbic acid
	1058 g	of sodium sulfite
	800 g	of hydroxypropylcellulose
15	1300 g	of corn starch

The preparation was carried out as described in Example 2, but by using a 5.625% aqueous hydroxypropylmethylcellulose solution as the coating agent.

20 **Example 6:** *Preparation of Dye Pellets by the Top Spray Method*

Mixture A

25	7.2 g	of 5-amino-2-methylphenol
	16.0 g	of 2,5-diaminotoluene sulfate
	4.0 g	of 2-amino-4-(β-hydroxyethylamino)anisole sulfate
	3.0 g	of ascorbic acid
	4.0 g	of sodium sulfite
30	965.8 g	of hydrolyzed corn starch (oligosaccharide)

The mixture was pelletized as described in Example 1 with 563 g of a 20% aqueous polyvinylpyrrolidone solution.

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Example 7: *Preparation of Dye Pellets by the Top Spray Method*

<u>Mixture A</u>	879 g	of dextrose
5 <u>Mixture B:</u> (dispersion)	30 g 500 g	of 2-amino-6-chloro-4-nitrophenol of a 20% aqueous polyvinylpyrrolidone solution (mol. wt. = 30,000 g/mol)

The mixture was pelletized as described in Example 1, but by using the afore-described mixture
10 (B) as spraying solution.

Example 8: *Preparation of Dye Pellets by the Top Spray Method*

<u>Mixture A:</u>	693.7 g	of dextrose
15 <u>Mixture B:</u> (dispersion)	20.8 g 5.5 g 400.0 g	of 4-(β-hydroxyethylamino)-3-nitrophenol of 2-hydroxyethylpicramic acid of 20% aqueous polyvinylpyrrolidone solution (mol. wt. = 30,000 g/mol)

The mixture was pelletized as described in Example 1, but by using the afore-described mixture
20 (B) as spraying solution.

Example 9: *Preparation of Dye Pellets by the Top Spray Method*

<u>Mixture A:</u>	721.6 g	of dextrose
30 <u>Mixture B:</u> (dispersion)	17.0 g 2.0 g 7.6 g 2.2 g 2.4 g 0.2 g 3.0 g 4.0 g 80.0 g 60.0 g 500.0 g	of 2,5-diaminotoluene sulfate of resorcinol of 2-methylresorcinol of 2-amino-6-chloro-4-nitrophenol of 6-amino-m-cresol of 4-amino-2-hydroxytoluene of ascorbic acid of sodium sulfite of alanine of glycine of 20% aqueous polyvinylpyrrolidone solution (mol. wt. = 30,000 g/mol)

Mixture (A) was pelletized as described in Example 1, but by using the afore-described Mixture (B) as spraying solution.

Example 10: *Creamy Hair Colorant*

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Cream base

	8.70 g	of cetylstearyl alcohol
	2.30 g	of glyceryl stearate (self-emulsifying)
	0.80 g	of lanolin
10	3.80 g	of lanolin alcohol
	1.42 g	of sodium cetylstearylsulfate
	0.07 g	of formaldehyde
	0.01 g	of tocopherol
	0.20 g	of perfume
15	10.00 g	of ammonia
	to 100.00 g	water

The afore-described cream base was prepared by the conventional hot-emulsification method. Before use, it was mixed with the dye pellets in an appropriate ratio as in one of Examples 1, 2, 3, 20 7, or 8 in a dye cup or shaking bottle.

Example 11: *Oxidation Hair Colorant*

Hydrogen Peroxide Emulsion

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	9.00 g	of hydrogen peroxide
	1.80 g	of cetylstearyl alcohol
	3.30 g	of polyvinylpyrrolidone-styrene copolymer
	0.20 g	of disodium phosphate
30	0.20 g	of sodium laurylsulfate
	0.10 g	of salicylic acid
	0.08 g	of phosphoric acid
	to 100.00 g	water

35 The above-described hydrogen peroxide emulsion was prepared by the conventional hot-emulsification method. Just before use, this hydrogen peroxide emulsion was mixed with dye pellets as in Example 5, 6 or 9 in a dye cup or a shaking flask.

Unless otherwise indicated, all percentages are by weight.